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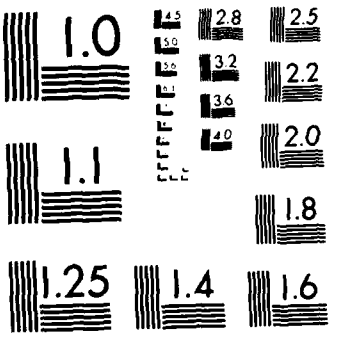

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Nitrocompounds, mixed "fluoroacid" transfer nitration, N-nitroimidazole, aromataic nitration, solid acid catalysis.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

New methods for preparation of nitrocompounds were studied including nitration with nitric-fluorosulfuric acid, transfer nitrations with N-nitropyrazole and-imidazole, solid superacid (Nafion-H) catalyzed nitrations and reactions with nitronium salts.

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Summary of Technical Report

Reference: Research Agreement No. DAAG29-82-K-0009
Completed on November 14, 1984

A new preparative nitration method using mixed "fluoroacid", FSO_3H-HNO_3 was developed, for the nitration of benzene to trinitrobenzene (TNB), of toluene to trinitrotoluene (TNT), as well as related polynitration of homologous alkylbenzenes. The system was also studied in conjunction with BF_3 as a dehydrating agent. Eliminating the use of anhydrous HF and replacing it with easy to handle FSO_3H is of substantial preparative advantage. The system is superior to mixed acid (HNO_3-H_2SO_3) and HNO_3-oleum systems, as the latter are also strong oxidizing agents and lead, particularly under forcing polynitration conditions, to oxidative degradations.

Covalent new mixed anhydrides of nitric acid with trifluoromethanesulfonic acid and fluorosulfonic acid were studied as nitrating agents, and found effective in aromatic nitrations.

Two new BF_3 catalyzed nitrating systems, N-nitropyrazole/BF_3 and $AgNO_3/BF_3$ were developed and studied in aromatic nitration.

N-nitropyrazole in the presence of Lewis or Bronstead acid catalysts was found to be an effective transfer nitrating agent for aromatic substrates. The nature of the acid catalyst affects both substrate and positional selectivities of the nitration of alkylbenzenes. No relationship was found between substrate and positional selectivities, which are considered to be determined in two separate steps.

Transfer nitrations were also studied with N-nitroimidiazole and pyrazole, and nitratotrimethoxyphosphonium salts. These new reagents give improved selectivities in transfer nitration reactions.

The use of pyridinium polyhydrogen fluoride as solvent medium for nitronium salt nitration of aromatics was found to be a substantially improved new nitration medium.

Pyridine-polyhydrogen fluoride-nitric acid or sodium nitrate were found convenient new nitrating system for aromatics. The systems are easy to handle and give good yields.

Electrophilic C-nitration of 2,6-di-tert-butylpyridine was achieved in the 4-position and that of 2,4,6-tri-tert-butylpyridine in the 3-position.

Benzene, alkylbenzenes, halobenzenes and anisole were nitrated with silver nitrate/boron trifluoride in acetonitrile solution. Correlation of competitive rates with π and σ-complex stabilities indicated that the transition state of highest energy lies relatively early on the reaction coordinate. Data indicate that nitrations occur via a polarized complex of the nitrating agent with the catalyst undergoing nucleophilic displacement by the aromatic substrate.

Significant new results were obtained in carrying out electrophilic aromatic nitrations over solid superacidic catalysts, such as the H-form of Nafion, a perfluorinated sulfonic acid resin. The acidity of this solid acid catalyst exceeds that of sulfuric acid and allows efficient nitrations to be carried out with various nitrating agents without the use of a liquid acid system (such as sulfuric acid). There is no need of aqueous-caustic work up or acid disposal. Obvious advantages are foreseen for a wide variety of applications.

Alkylbenzenes, halobenzenes and naphthalene were nitrated with nitric acid under azeotropic conditions of removal of water with Hg^{++} impregnated Nafion-H perfluorinated sulfonic acid resin catalyst. The isomer ratios of nitroalkylbenzenes showed differences from conventional acid catalyzed nitrations yielding larger amounts of the less hindered isomer.

The reaction of nitroalkanes with iodotrimethylsilane was investigated and the scope of the synthetically useful transformation established.

The oxidation of sulfoxides to sulfides with nitronium salts was studied. This is of particular interest in regard to the ambident reactivity of the nitronium ion.

A comprehensive review on our recent studies on preparative and mechanistic aspects of nitration was published, summarizing results of the last five years of ongoing work supported by Army Research in our laboratory.

Writing of a monograph on nitration is in progress. The book is scheduled to be published by Academic Press in 1985.

Scientific Personnel Supported (in part) and Degrees Awarded:

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Hans Doggweiler, post-doctoral associate

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Joseph G. Shih, graduate student, Ph.D. 1984

List of Publications under ARO Sponsorship:

Olah, G.A., Narang, S.C., and Fung, A.P. Aromatic Substitution. 47. Acid Catalyzed Transfer Nitration of Aromatics with N-Nitropyrazole, J.Org. Chem., 46, 2706 (1981).

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